Studies on the Derivatives of Biphenylene Oxide. VI. 4-Nitrobiphenylene Oxide and its Derivatives.

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In the previous communication[1], it was shown by the present author that the mononitrobiphenylene oxide melting at about 91–93° (uncorr.), which was obtained from the nitration products of biphenylene oxide by fractional distillation and fractional crystallization, should be 4-nitrobiphenylene oxide, not being 1-nitrobiphenylene oxide. This conclusion, however, was nothing but an assumption based upon the tendency of substitution of the hydrogen atoms of biphenylene oxide by the nitro group, because till that time 1-nitrobiphenylene oxide had not yet been prepared by anyone. In the recent investigation[2] 1-nitrobiphenylene oxide was prepared, and lately a pure mononitrobiphenylene oxide melting at 126–126.5° (corr.) was isolated by the same author from the above-mentioned fraction melting at 91–93°, by means of repeated recrystallization from glacial acetic acid for the removal of contaminated 2- and 3-nitrobiphenylene oxides. This newly isolated nitro compound was ascertained to be 4-nitrobiphenylene oxide by the depression of its melting point then occurred when mixed with 1-, 2- or 3-nitrobiphenylene oxide. Judging from the yields of 2-nitro (71%), 3-nitro (10%), 4-nitro (crude product, 5%; purified product, 1%) and 1-nitro (none was isolated) compounds, the tendency of the introduction of the nitro group in the formation of the mononitrobiphenylene oxides must be in the order of the positions 2>3>4>1.

Amido-, acetamido-, dinitro-, trinitro-, tetranitro-, and bromonitrobiphenylene oxides were derived from 4-nitrobiphenylene oxide in confirmation of the last compound. The constitutons of those derivatives were determined, and then the physical properties and the absorption spectra of the four mononitrobiphenylene oxides and their corresponding derivatives were compared one another as in Tables 1–7 and Figs. 1–5 respectively, which will be utilized for the benefit of isolation and identification of those compounds.

The compounds obtained newly by the present author are asterisked in the above tables. Of those compounds, 6-bromo-1-nitro-, 6-bromo-3-nitro- and 6-bromo-4-nitro-biphenylene oxides were prepared from the corresponding nitro compounds by bromination in glacial acetic acid, and 4,6-dinitro-, 2,4,6-trinitro-, and 2,4,6,7-tetranitro-biphenylene oxides, from 4-nitrobiphenylene oxide by successive nitrations. The constitution of those new compounds were established as follows.

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(1) S. Yamashiro, *J. Chem. Soc. Japan*, **57** (1936), 715.
(2) S. Yamashiro, *ibid.*, **59** (1938), 950.

Comparison of the physical properties.

Table 1. Mononitrobiphenylene oxides.

Compound	M.p.(corr.)	Crystal (Crystallizing solvent)	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Actone	Acetic acid	Ethyl acetate
1-Nitro	138 –139°	Pale yellow needle (Ethanol)	d	e	e	e	e	m	m	e	m	e
2-Nitro	186 –186.5°	Pale yellow needle (Acetic acid)	d	d	m	m	m	d	d	m	m	m
3-Nitro	158.5–159.5°	Pale yellow needle (Ethanol)	d	d	m	e	e	m	m	e	m	e
*4-Nitro	126 –126.5°	Pale yellow needle (Acetic acid)	m	e	e	e	e	m	m	e	m	e

Table 2. Amidobiphenylene oxides.

1-Amido	118 119°	Colourless needle (Ethanol)	e	e	e	e	e	e	e	e	e	e
2-Amido	99°	Colourless needle (Ethanol-water)	d	e	e	e	e	e	e	e	e	e
3-Amido	125 –125.5°	Colourless needle (Ethanol-water)	m	e	e	e	e	e	e	e	e	e
*4-Amido	113.5–114.5°	Colourless needle (Ligroin)	m	e	e	e	e	e	e	e	e	e

Table 3. Acetamidobiphenylene oxides.

1-Acetamido	235 –236°	Colourless short needle (Ethanol-water)	d	d	e	e	e	e	e	e	e	e
2-Acetamido	182°	Colourless needle (Ethanol-water)	d	e	m	e	e	e	e	e	e	e
3-Acetamido	166 –166.5°	Colourless needle (Ethanol)	d	d	m	m	m	m	m	e	e	e
*4-Acetamido	259 –260°	Colourless long needle (Ethanol)	d	d	d	e	m	m	m	e	m	e

Table 4. Dinitrobiphenylene oxides.

Compound	M.p. (corr)	Crystal (Crystallizing solvent)	Solubility (e : easily soluble, m : moderately soluble, d : difficultly soluble ; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Actone	Acetic acid	Ethyl acetate
1,6-Dinitro	263 -264°	Colourless needle (Acetic acid)	d	d	d	m	m	d	d	m	m	m
2,6-Dinitro	255 -256°	Pale yellow needle (Benzene)	d	d	d	m	m	d	d	m	m	m
3,6-Dinitro	329 -330°	Colourless needle (Acetone)	d	d	d	m	m	d	d	m	m	m
*4,6-Dinitro	241 -242°	Colourless needle (Acetic acid)	d	d	d	e	m	d	d	m	m	m
1,8-Dinitro	351 -352°	Pale yellow needle (Ethanol)	d	d	d	d	d	d	d	d	d	d
2,7-Dinitro	326 -327°	Colourless needle (Acetic acid)	d	d	d	d	d	d	d	d	d	d

Table 5. Trinitrobiphenylene oxides.

1,3,6-Trinitro	312 -313°	Small colourless rhombic plate (Benzene)	d	d	d	d	m	d	d	m	m	m
1,3,8-Trinitro	260 -261°	Pale yellow hexagonal plate (Acetone-ethanol)	d	d	d	e	e	d	d	e	e	e
2,3,6-Trinitro	237 -238°	Pale yellow hexagonal plate (Benzene)	d	d	d	d	m	d	d	e	m	e
2,3,7-Trinitro	276.5-277.5°	Pale yellow needle (Benzene)	d	d	d	e	m	d	d	e	e	e
*2,4,6-Trinitro	207 -208°	Pale yellow needle (Ethanol)	d	d	d	e	e	m	m	e	e	e

Table 6. Tetranitrobiphenylene oxides.

Compound	M.p. (corr.)	Crystal (Crystallizing solvent)	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble; e>m>d.)									
			Ligroin	Ether	Carbon tetrachloride	Chloroform	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
1,3,6,8-Tetranitro	262 -263°	Colourless prism (Acetic acid)	d	d	d	d	m	d	d	e	m	e
1,3,6,7-Tetranitro	249 -250°	Colourless needle (Benzene)	d	d	d	d	m	m	m	e	e	e
2,3,6,7-Tetranitro	285 -286°	Colourless needle (Benzene)	d	d	d	d	m	d	d	e	m	e
*2,4,6,7-Tetranitro	253 -254°	Colourless rectangular plate (Benzene)	d	d	d	d	m	d	d	e	m	m

Table 7. Bromonitrobiphenylene oxides.

6-Bromo-1-nitro	231 -232°	Small colourless nee le (Carbon tetrachloride)	d	d	m	e	e	d	m	e	m	e
6-Bromo-2-nitro	258 -259°	Colourless needle (Acetic acid)	d	d	m	m	m	d	d	m	m	m
*6-Bromo-3-nitro	226 -227°	Colourless rhombic plate (Acetone)	d	d	m	e	e	d	d	m	m	m
*6-Bromo-4-nitro	189.5-190.5°	Yellow long needle (Acetic acid)	m	e	e	e	e	m	m	e	m	e

The bromination of biphenylene oxide in glacial acetic acid takes place, as shown in Part V[3], smoothly at the position 3, not at 1, 2, and 4. This directive action in one phenylene residue of biphenylene oxide must be strengthened by the introduction of a negative nitro group in the other phenylene residue. On the other hand, the bromination of mononitro- and dinitro-biphenylene oxides were examined by the author to be found that no bromine atom can be introduced smoothly into the phenylene residue, in which a nitro group is present. That is to say, the mononitro compounds gave only monobromo derivatives in good yield, whereas the dinitro compounds which have each of the nitro groups in both phenylene residues of a molecule, as in 1,8-, 2,6-, 2,7-, and 3,6-dinitro compounds, gave no bromo derivatives. From those experimental results, it can be concluded that the bromination of x-nitrobiphenylene oxide (x=1, 2, 3, or 4) gives 6-bromo-x-nitrobiphenylene oxide as a main product. A support of this view can be found in the paper communicated by H. Gilman and his co-workers[4], who had obtained 6-bromo-2-nitrobiphenylene oxide from 2-nitrobiphenylene oxide.

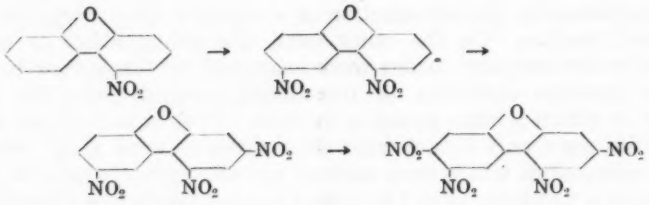
The dinitrobiphenylene oxide derived from 4-nitrobiphenylene oxide must have each of the nitro groups in both phenylene residues separately, forming 4,6-dinitrobiphenylene oxide, because this dinitro compound gave no bromo derivative by bromination. Among the positions (2, 3, and 7) which are free and more active to be taken in the nitration of the 4-6-dinitro compound, 2 and 3 are more favourable than 7 for the introduction of the third nitro group owing to the meta-directive influence of the nitro groups already present in the molecule, because either of the nitro groups of 4,6-dinitrobiphenylene oxide exerts a favourable directipe influence to the position 2 or 3, while neither of them exerts a similar influence to the position 7. Of the positions 2 and 3 again, the former is more favourable than the latter for the introduction of the third nitro group, as in the case of nitration of biphenylene oxide, even if the directive influence of the nitro group at the position 4 causing the nitration at the position 2 is equal to that of the nitro group at the position 6 which causes the nitration at 3. From these considerations, it can be concluded that the trinitro compound obtained from 4,6-dnitrobiphenylene oxide is 2,4,6-trinitrobiphenylene oxide. The tetranitro compound obtained as a main product from the last compound must be 2,4,6,7-tetranitrobiphenylene oxide (along with it 2,4,6,8-tetranitrobiphenylene oxide may be formed, by the bye), because it gave no higher polynitro compound, as in the case of nitration of 1,3,6,8-, 1,3,6,7-, and 2,3,6,7-tetranitrobiphenylene oxides, even when it was heated for a long time with a large excess of fuming nitric acid (d 1.52). On the contrary, if the tetranitro compound were 2,3,4,6-tetranitro-biphenylene oxide, it would give 2,3,4,6,7- and 2,3,4,6,8-pentanitrobiphenylene oxides, as in the case of nitration of 1,3,6- and 2,3,6-trinitrobiphenylene oxides[5], the former of which gave 1,3,6,7- and 1,3,6,8-tetranitro compounds and the latter, 2,3,6,7- and 2,3,6,8-tetranitro

(3) S. Yamashiro, this Bulletin, **15** (1941), 6.

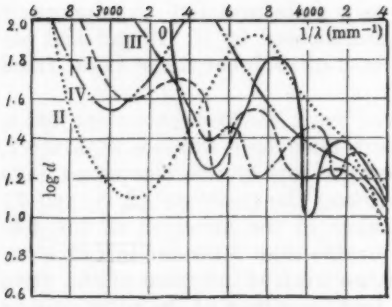
(4) H. Gilman, G. E. Brown, W. B. Bywater and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56** (1934), 2476.

(5) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 448, 450.

compounds. Judging from the reasoning given above, the main reactions of the successive nitrations of 4-nitrobiphenylene oxide may proceed as follows:

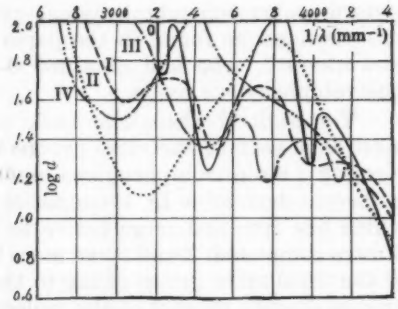


Comparison of the absorption curves.



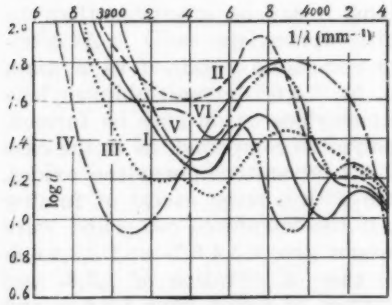
0 (——) Biphenylene oxide.
I (– – –) 1-Nitrobiphenylene oxide.
II (····) 2- ,, ,, .
III (–·–) 3- ,, ,, .
IV (–···) 4- ,, ,, .

Fig. 1. Mononitrobiphenylene oxides. M/10000 alcoholic solutions.



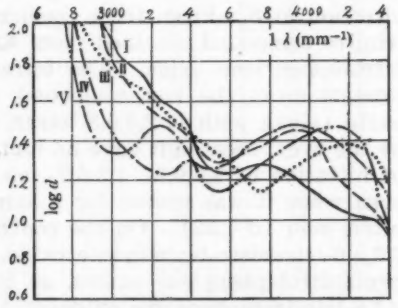
0 (——) 3-Bromobiphenylene oxide.
I (– – –) 6-Bromo-1-nitrobiphenylene oxide.
II (····) 6- ,, -2- ,, ,, .
III (–·–) 6- ,, -3- ,, ,, .
IV (–···) 6- ,, -4- ,, ,, .

Fig. 2. Bromonitrobiphenylene oxides. M/10000 alcoholic solutions.



I (——) 1,6-Dinitrobiphenylene oxide.
II (– – –) 1,8- ,, ,, .
III (····) 2,6- ,, ,, .
IV (–·–) 2,7- ,, ,, .
V (–···) 3,6- ,, ,, .
VI (–····) 4,6- ,, ,, .

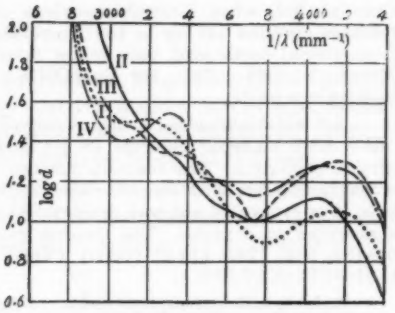
Fig. 3. Dinitrobiphenylene oxides. M/10000 alcoholic solutions.



I (——) 1,3,6-Trinitrobiphenylene oxide.
II (– – –) 1,3,8- ,, ,, .
III (····) 2,3,6- ,, ,, .
IV (–·–) 2,3,7- ,, ,, .
V (–···) 2,4,6- ,, ,, .

Fig. 4. Trinitrobiphenylene oxides. M/10000 alcoholic solutions.

Among the mononitrobiphenylene oxides, the 1- and 3-nitro compounds having a nitro group at the *o*- and *p*-positions respectively to the ring-forming oxygen atom of biphenylene oxide give two resembling absorption curves, which have three characteristic absorption bands in each other (Fig. 1, Curves I and III), whereas the 2- and 4-nitro compounds, which have both a nitro group at the *m*-position to the ring-forming oxygen atom, give also two resembling curves which have both only one wide characteristic absorption band respectively (Fig. 1, Curves II and IV). The absorption bands of the 1- and 4-nitro compounds are more bathochromic than the corresponding bands of the 3- and 2-nitro isomerides.



I (——) 1,3,6,7-Tetranitrobiphenylene oxide.
II (– – –) 1,3,6,8- „ „ .
III (····) 2,3,6,7- „ „ .
IV (–·–) 2,4,6,7- „ „ .

Fig. 5. Tetranitrobiphenylene oxides. M/10000.

As seen from the comparison between the absorption curve of the *x*-nitrobiphenylene oxide (*x*=1, 2, 3 or 4) and that of the corresponding 6-bromo-*x*-nitro compound (Fig. 1, Curves I–IV and Fig. 2, Curves I–IV), the introduction of a bromine atom into the position 6 of the *x*-nitro compound exerts no remarkable influence upon the absorption spectrum of the parent compound.

Similarity of the absorption curves can be found also in the case of dinitrobiphenylene oxides, namely, among the 1,6-, 1,8-, and 3,6-dinitro compounds on one hand (the compounds having nitro groups at the *o,p'*-, *o,o'*- and *p,p'*-positions respectively to the ring-forming oxygen atom; Fig. 3, Curves I, II, and V), and between the 2,6-, and 4,6-dinitro compounds on the other (the compounds substituted at the *m,p'*-positions to the ring-forming oxygen atom; Fig. 3, Curves III and VI). But the 2,7-dinitro compound (the *m,m'*-substituted compound; Fig. 3, Curve IV) gives a curve of special type which is analogous to that of 2-nitrobiphenylene oxide.

In the curves of the trinitro- and tetranitro-biphenylene oxides, no analogy can be found among them, except for those of the 2,4,6-trinitro and 2,4,6,7-tetranitro compounds, both of which give a characteristic absorption band at about $1/\lambda$ (mm^{-1}) 3000, owing to the presence of a nitro group at the position 4 of them.

Experimental.

4-Nitrobiphenylene oxide. As shown in Part I,[1] the reaction products obtained by treating biphenylene oxide (100 g.) with fuming nitric acid (d 1.52; 300 c.c.) in glacial acetic acid (100 c.c.) were recrystallized from acetic acid, when 2-nitrobiphenylene oxide (Yield 71%) was isolated. The mother-liquor was diluted with water precipitating the other components which were fractionated by repeated crystallizations from alcohol and by fractional distillations under the reduced pressure. The fraction distilled out at about the temperature 180–185°/3 mm was again recrystallized

from alcohol, when 3-nitrobiphenylene oxide was isolated (Yield 10%). Next, the fraction distilled out up to the temperature 180°/3 mm was repeatedly recrystallized from glacial acetic acid, pale yellow needles melting at 126–126.5° (corr.) (Yield 1%. Found : N, 6.64. Calc. for $C_{12}H_7ONO_2$: N, 6.57%). The last compound is 4-nitrobiphenylene oxide.

4-Amidobiphenylene oxide. 4-Nitrobiphenylene oxide (2 g.) was reduced by heating it with stannous chloride (8 g.) and concentrated hydrochloric acid (40 c.c.) in alcohol (300 c.c.). The reaction mixture was evaporated, diluted with water and made strongly alkaline with caustic soda solution precipitating the reduced substance. The base thus separated out was dried quickly, extracted with benzene and the extract was evaporated to dryness. The residue was then recrystallized from ligroin, colourless needles, m.p. 113.5–114.5° (corr.) (Yield 1.86 g., 97.5%. Found : N, 7.70. Calc. for $C_{12}H_7ONH_2$:N, 7.69%.).

4-Acetamidobiphenylene oxide. 4-Amidobiphenylene oxide (1 g.) was warmed for a short time with a mixture of acetic anhydride (1 c.c.) and acetic acid (5 c.c.), and then diluted with water precipitating the reaction product, which was recrystallized from alcohol, colourless needless, m.p. 259–260° (corr.) (Yield 1.2 g., 97.6%. Found : N, 6.32. Calc. for $C_{12}H_7ONHCOCH_3$: N, 6.23%.).

6-Bromo-1-nitrobiphenylene oxide. 1-Nitrobiphenylene oxide (1 g.) was heated for 5 hours with a large excess of bromine (3. g.) in boiling glacial acetic acid (30 c.c.). After dilution with water, the reaction product separated out was recrystallized from alcohol, colourless needles, m.p. 231–232° (corr.) (Yield 1.28 g., 93.4%. Found : N, 4.81; Br, 27.34. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%.).

6-Bromo-2-nitrobiphenylene oxide. 2-Nitrobiphenylene oxide (1 g.) was brominated by the method described by H. Gilman and his co-workers[3] and the reaction product was recrystallized from glacial acetic acid, colourless needles, m.p. 258–259° (corr.) (Yield 1.15 g., 84%. Found:N, 4.82; Br, 27.30. Calc. for $C_{12}H_6OBrNO_2$:N, 4.79; Br, 27.36%.).

6-Bromo-3-nitrobiphenylene oxide. 3-Nitrobiphenylene oxide (1 g.) was brominated as in the case of bromination of 1-nitrobiphenylene oxide and the reaction product was recrystallized from acetone, colourless rhombic plates, m.p. 226–227° (corr.) (Yield 1.33 g., 97%. Found:N, 4.86. Br, 27.29. Calc. for $C_{12}H_6OBrNO_2$:N, 4.79; Br, 27.36%.).

6-Bromo-4-nitrobiphenylene oxide. 4-Nitrobiphenylene oxide (1 g.) was also brominated as in the case of bromination of 1-nitrobiphenylene oxide and the reaction product obtained was recrystallized from glacial acetic acid, long yellow needles, m.p. 189.5–190.5° (corr.) (Yield 1.20 g., 87.5%. Found : N, 4.84; Br, 27.41. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%.).

4,6(or 3,5)-Dinitrobiphenylene oxide. 4-Nitrobiphenylene oxide (2.13 g.) was treated with fuming nitric acid (d 1.45; 20 c.c.) at the room temperature. After 20 minutes, the reaction mixture was poured into water and the reaction product thus separated out (2.5 g.) was recrystallized from glacial acetic acid, colourless needles, m.p. 241–242° (corr.) (Yield 1.70 g., 66%. Found : N, 10.71. Calc. for $C_{12}H_6O(NO_2)_2$: N, 10.85%.). This compound gave no brominated product even when it was heated for a long time with a large excess of bromine in boiling acetic acid.

2,4,6-Trinitro- and 2,4,6,7-tetranitro-biphenylene oxides. 4,6-Dinitrobiphenylene oxide (1.29 g.) was heated for 30 minutes with fuming nitric acid (d 1.52; 13 c.c.) and then diluted with water, separating out white precipitates. The reaction products were filtered, dried (Yield 1.58 g.) and extracted with chloroform. The residue was recrystallized from benzene, colourless rectangular plates, m.p. 253–254° (corr.) (Yield 0.196 g., 15.2%. Found : N, 16.12. Calc. for $C_{12}H_4O(NO_2)_4$:N, 16.10%.). The chloroform extract was evaporated to dryness and, after being extracted with 1% hot caustic soda solution to remove the contaminated tetranitro compound, the residue was recrystallized from acetone-alcohol, pale yellow needles, m.p. 207–208°(corr.) (Yield 0.294 g., 22.8%. Found : N, 13.93. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%.). The last trinitro compound was heated for 3 hours with a large excess of fuming nitric acid (d 1.52), when the foregoing tetranitro compound was obtained, but none of the pentanitro compound was isolated. The trinitro and tetranitro compounds obtained here are, as is made clear by the reasoning given above, 2,4,6-trinitro- and 2,4,6,7,-tetranitrobiphenylene oxides respectively.

Summary.

(1) 4-Nitrobiphenylene oxide was isolated in a pure state from the nitration products of biphenylene oxide and the amido, acetamido, dinitro, trinitro, tetranitro and bromonitro derivatives were prepared from it. The constitutions of the latter four derivatives were established.

(2) The physical properties, especially the absorption spectra, of those newly obtained compounds and the corresponding compounds derived from 1-, 2- and 3-nitrobiphenylene oxides were comparatively studied.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of the Osaka Imperial University and Shigemi Oba, the principal of the Yonezawa Higher Technical School, for their kind advices and encouragements. A part of the expense of this investigation has been defrayed from the grant of the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the author wishes to record his thanks.

Yonezawa Higher Technical School.

The Copper Content of the Hot Springs of Yunohanazawa, Hakone, Kanagawa Prefecture, and that of the Hot Springs of Osoreyama, Aomori Prefecture.

By Kazuo KURODA.

(Received February 22, 1941.)

In a previous paper[1], the author gave the results obtained, up to the time of publication, on the copper content of Japanese mineral springs. The copper content of a number of mineral springs was estimated by H. Fischer's diphenylthiocarbazone (dithizone) method[2]. The writer's recent work, the results of which are given in this paper, concerns the determination of this element by the polarographic method.

(1) Determination of Copper by the Polarographic Method. For the polarographic determination of copper, the method of M. Shikata,

(1) K. Kuroda, this Bulletin, **15** (1940), 439.
(2) H. Fischer, *Angew. Chem.*, **47** (1934), 685; **50** (1937), 919.

I. Tachi, and N. Hozaki[3] was at first tried, but the writer failed to detect the presence of copper in the hot springs by this method. The second method adopted was that of K. Heller, G. Kuhla, and F. Machek[4], in which the copper in mineral waters is extracted with a carbon tetrachloride solution of dithizone. Notwithstanding the most scrupulous care exercised, the search ended in failure. The chief cause of failure probably lay in the presence of a large amount of iron in the mineral waters. After several trials, the following procedure, in which the large excess of iron is removed by ammonia prior to the extraction of copper by the carbon tetrachloride solution of dithizone, was found to be satisfactory for determining the minute traces of copper in acid alum-vitriol springs:

Add nitric acid to 500 c.c. of the mineral water and boil in order to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) in slight excess and 5 c.c. of saturated ammonium carbonate solution. Warm and filter. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1), and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with nitric acid, and evaporate to dryness. Dissolve the residue in nitric acid, adjust to *p*H 3. Shake with successive 10 c.c. portions of the purified carbon tetrachloride solution of dithizone. Continue the extraction until the carbon tetrachloride layer remains green. Add 10 c.c. of conc. nitric acid and 10 mg. of sodium nitrate to the combined extracts and evaporate to dryness. Dissolve the residue in 10 c.c. of "Grundlösung A"[5] (170 g. $NaNO_3$+200 c.c. of gelatine solution (2%)+1800 c.c. H_2O). The solution is transferred to a small electrolysis vessel and polarographically examined. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amount of copper salt in "Grundlösung A".

The efficacy of the method was tested by adding known amounts of standard copper sulphate solution to 500 c.c. of water and submitting the solution to complete extraction, and polarographic determination with the following results:

Table 1.

No.	Height of wave (mm.)	Sensitivity
(1) 500 γ copper.	54	1/10
(2) Cu (500 γ) added to distilled water (500 c.c.). Extracted by dithizone.	53	1/10
(3) Cu (500 γ) added to the Yoemon-Yu spring water (500 c.c.). Extracted by dithizone.	54	1/10

(3) M. Shikata, I. Tachi and N. Hozaki, *Bull. Agr. Chem. Soc. Japan*, **3** (1927), 883.
(4) K. Heller, G. Kuhla and F. Machek, *Mikrochemie*, **23** (1937), 78.
(5) H. Hohn, "Chemische Analysen mit dem Polarographen," Berlin (1937), 41.

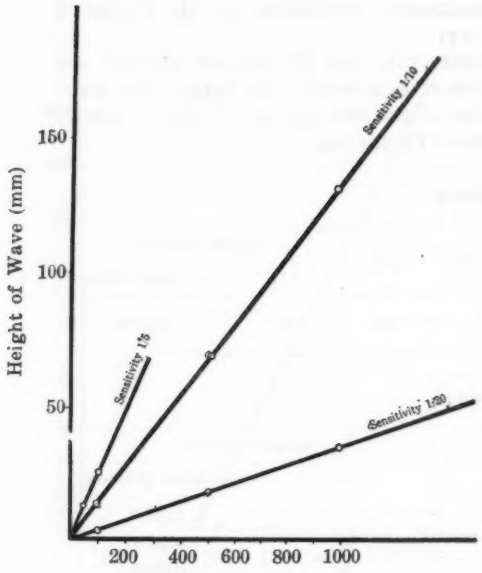


Fig. 1.

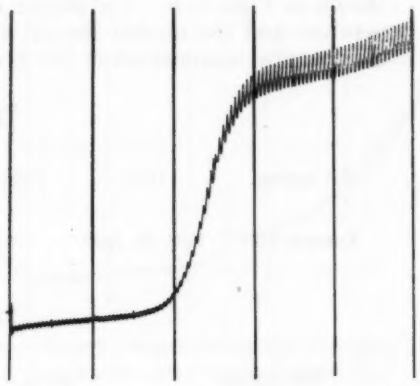


Fig. 2. Wave due to 500 γ of copper in "Grundlösung A". Sensitivity 1/10.

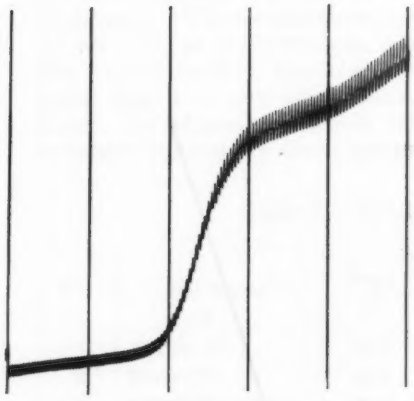


Fig. 3. 500 γ of copper was added to 500 c.c. of water. Extracted with carbon tetrachloride solution of diphenylthiocarbazone. "Grundlösung A". Sensitivity 1/10.

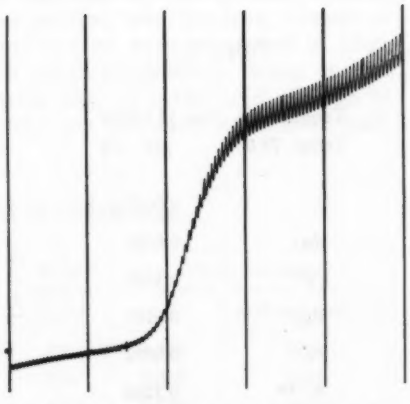


Fig. 4. 500 γ of copper was added to 500 c.c. of "Yoemon-Yu" spring. Extracted with carbon tetrachloride solution of diphenylthiocarbazone. "Grundlösung A". Sensitivity 1/10.

(2) Copper Content of the Hot Springs of Yunohanazawa, Hakone, Kanagawa Prefecture. The copper content of the Yoemon-Yu hot spring was polarographically estimated, with the result shown in Table 2, and

that of the hot springs of Yunohanazawa, estimated by H. Fischer's dithizone method[2], shown in Table 3.

The relations between temperature, *p*H, and the copper content are shown in Figs. 5, 6. The copper content is greater, the higher the temperature and the smaller the *p*H value of the hot spring. Table 4. shows the chemical composition of the Yoemon-Yu spring.

Table 2.

Hot spring	Date	Temp. (°C)	*p*H	Copper content	
				γ/l.	% (total residue)
Yoemon-Yu	Feb. 19, 1939	74.5	2.2	45	0.0026

Table 3.

Hot spring	Date	Copper content	
		γ/l.	% (total residue)
(1) Gongen-Yu	Aug. 20, 1938	7.1	0.0009
(2) Gongen-Yu	Aug. 26, 1939	10	0.0008
(3) Kōbō-Yu	Aug. 20, 1938	5	0.0005
(4) Yoemon-Yu	Aug. 20, 1938	90	0.0045
(5) Yoemon-Yu	Feb. 19, 1939	45	0.0026
(6) Daruma-Zigoku	Aug. 20, 1938	163	0.0081

Table 4.

Yoemon-Yu. Dec. 11 (1938) Temp. 78.0°C. *p*H 2.3	
K^+	0.0029 g./l.
Na^+	0.0329
Ca^{++}	0.1029
Mg^{++}	0.0131
Fe^{++}	0.0392
Al^{+++}	0.1204
SO_4^{--}	1.0366
Cl^-	0.0026
H_2SiO_3	0.3674
H_2S	trace
	1.7180 g./l.

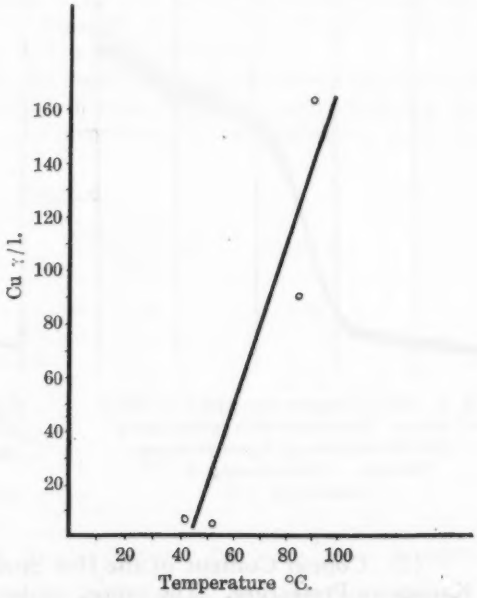


Fig. 5. Temperature and Copper Content.

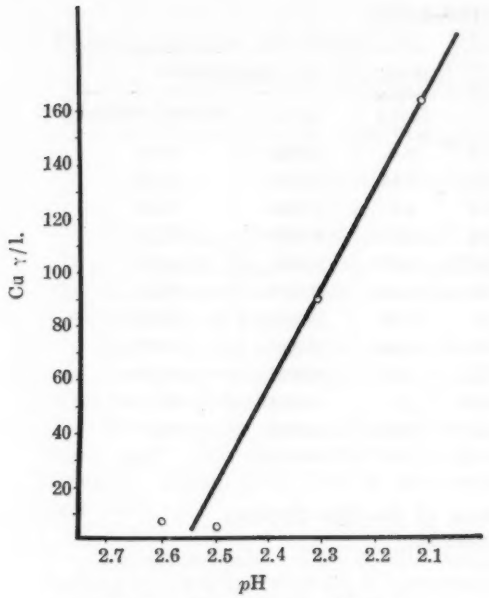


Fig. 6. *p*H and Copper Content.

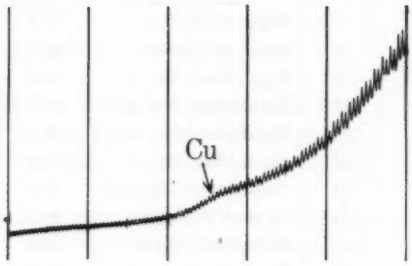


Fig. 7. Wave due to 45γ of copper extracted from the "Yoemon-Yu" spring. "Grundlösung A". Sensitivity 1/10.

(3) Copper Content of the Hot Springs of Osoreyama, Aomori Prefecture. The temperature, *p*H, total residue, and the iron content of the hot springs of Osoreyama, Aomori prefecture, were measured in 1940. The copper content was also estimated polarographically, when it was found that it is very small compared with that of other acid springs in Japan, the reason for which is probably the presence of considerable hydrogen sulphide in these springs[6].

Table 5. Hot Springs of Osoreyama.

No.	Hot spring	Temp. °C.	*p*H	Total residue (g./l.)	Iron content	
					g./l.	% (total residue)
1	Yakusi-Yu	70.0	1.8	3.2	0.025	0.78
2	Hie-no-Yu	89.5	1.9	5.25	0.018	0.34
3	Hurutaki-no-Yu	79.0	2.0	5.30	0.030	0.57
4	Hanazome-no-Yu	68.5	2.0	1.5	0.0013	0.087
5	Sintaki-no-Yu No. 1	83.0	2.2	4.2	0.0034	0.081
6	Sintaki-no-Yu No. 2	60.8	2.4	3.1	0.015	0.48

(6) As is shown in Table 2, the copper content of the Gongen-Yu spring and the Kōbō-Yu spring is very small compared with that of other hot springs in Yunohanazawa, the reason for which is also the presence of considerable hydrogen sulphide in these springs. The Gongen-Yu spring contains 51.9 mg. and the Kōbō-Yu spring 33.1 mg. per litre of hydrogen sulphide.

Table 5.—(*Concluded*)

No.	Hot spring	Temp. °C	pH	Total residue. (g./l.)	Iron content.	
					g./l.	% (total residue)
7	Tikusyo-Zigoku	23.5	2.2	0.4	0.0022	0.55
8	Sioya-no-Zigoku	98.5	2.4	6.05	0.0101	0.167
9	Zigokudani No. 1	97.5	2.4	2.2	0 0042	0.19
10	Zigokudani No. 2	95.5	2.4	2.6	0.0038	0.15
11	Zigokudani No. 3	93.8	2.5	1.6	0 044	2.75
12	Zigokudani No. 4	75.5	2.4	4.8	0.0106	0.22
13	Bakutiuti-no-Zigoku	97.5	4.1	11.45	0.0017	0.015
14	Syurao-no-Zigoku	99.0	5.6	14.40	0.0001	0.007
15	Hokke-no-Zigoku	82.8	5.8	2.3	0.0001	0.004
16	Lake Osoreyama	22.0	3.0	0.1	0.0001	0.1
17	Drinking water	14.0	4.8	0.03	0.0001	0.3

Table 6. Copper Content of the Hot Springs of Osoreyama.

	γ/l.	% (total residue)
No. 6	30	0.00026
No. 13	20	0.00065

Summary.

A method for the polarographic estimation of copper is described. The copper content of the hot springs of Yunohanazawa, Hakone, Kanagawa prefecture, and that of Osoreyama, Aomori prefecture, are polarographically estimated.

The writer expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The expenses in connexion with this study were defrayed from a grant received by Prof. Kimura from the Japan Society for the Promotion of Scientific Research, to which last the writer's thanks are also due.

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Polymerisation of Tung Oil. VII. Effects of Various Inorganic Substances upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

The effects of various inorganic substances upon the gelation of tung oil at elevated temperatures being little known, the author carried out this experiments to obtain the effects of inorganic substances upon the gelation time of tung oil.

Each of the reagents was added to tung oil with 10% by weight and the measurements were done at 273°C, and the results were compared with the blanc tests.

The reagents were pulverized as fine as possible and the sifted parts were used. The substances which affect the metallic net of the standard sieve, or which could not be pulverized were directly weighed into the test tube.

Experimentals. The results were shown in Tables 1 (substances having no or little effects), 2 (accelerating effects), 3 (retarding effects). The number in the Tables are the values calculated from $(t-t_0)/t_0$, where t and t_0 are the gelation times of tung oil added with reagents and that of the blanc test. Therefore the plus sign means the gelation retarding action and the minus sign, the gelation accelerating one.

Table 1.

$(t-t_0)/t_0$ (%)	Substances
0	Hg, Bi, $(NH_4)_2Cr_2O_7$.
0~+1.0	$Ba(NO_3)_2$, $Co(NO_3)_2$, K_2CrO_4, $Na_2C_2O_4$, KBr.
+1.0~2.0	KNO_3, $NaHPO_3 \cdot 3H_2O$ $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_3 \cdot 7H_2O$, NaBr, C_2O_4Ce.
+2.0~3.0	$AlK(SO_4)_2 \cdot 12H_2O$, NH_4Cl.
+3.0~4.0	Sb_2O_3, $PbCl_2$, KNO_2, Cr_2O_3, $Al_2(SO_4)_3 \cdot 18H_2O$.
+4.0~5.0	K_2SO_4, $CH_3COONa \cdot 3H_2O$, $BaSO_4$.
0~−1.0	Na_2SO_4, KI, $NaNO_3$, SnO_2, Al_2O_3, Sb.
−1.0~2.0	$CaCl_2 \cdot xH_2O$, $BaCl_2$, Hg_2Cl_2, $FeSO_4 \cdot 7H_2O$.
−2.0~3.0	$MnCl_2 \cdot 4H_2O$, $KHSO_4$, $Fe_2(SO)_3$, $MnSO_4 \cdot 4H_2O$, C_2O_4Pb, Lead Arsenate.
−3.0~4.0	Ni (plate), $CaSO_4$, ZnS, $(NH_4)ClO_4$.
−4.0~5.0	$Sr(NO_3)_2$, Cd, NaCl, $Cr(NO_3)_3$.

Table 2.

$(t-t_0)/t_0$ (%)	Substances
− 5∼ 10	$Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, $CdSO_4\cdot 8H_2O$, $(NH_4)_2SO_4$, $K_2Cr_2O_7$, $CuCl_2$, Cu_2Cl_2, $CrCl_3\cdot xH_2O$.
−10∼ 20	$Fe(NH_4)_2(SO_4)_2\cdot 12H_2O$, Zn, $HgSO_4$, $MgSO_4$, $CuSO_4\cdot 5H_2O$, $(Hg)_2CrO_4$.
−20∼ 30	NH_4NO_3, $KClO_3$, $(CH_3COO)_2Cu\cdot H_2O$.
−30∼ 40	CuO, Cu_2O, $Ni(NO_3)_2$, $Hg(NO_3)_2$, CH_3COOHg.
−40∼ 50	$Th(NO_3)_4\cdot 4H_2O$, HgO, $UO_2(NO_3)_2$, $CoCl_2\cdot 6H_2O$.
−50∼ 60	$Bi(NO_3)_2$.
−70∼ 80	Na.
−80∼ 90	$HgCl_2$.
−90∼100	$ZnCl_2$, ICl_3, $FeCl_3\cdot 6H_2O$, $AlCl_3$, I_2, $SnCl_4$ $POCl_3$.

Generally halides have very strong gelation accelerating actions.

Table 3.

$(t-t_0)/t_0$ (%)	Substances
+ 5∼ 10	$(NH_4)_2S_2O_8$, $CuCO_3\cdot Cu(OH)_2$, $NaHPO_4$, Uranium acetate, KCNS, Fe, Cu, $AgNO_3$, Sn.
+10∼ 20	LiCl, CoO, NaOCl, $Mn(OH)_2$, Mn-Borate.
+20∼ 30	ZnO, Al.
+40∼ 50	$(HCOO)_2Pb$, Mg, KCN, Na-Oleate, Al-Stearate.
+50∼ 60	$Ca(NO_3)_2$, $NaHCO_3$, $KMnO_4$.
+90∼100	$SbCl_3$.
+100∼200	$Mg(NO_3)\cdot xH_2O$, $Pb(NO_3)_2$, $H_3AsO_4\,1/2H_2O$, Animal Charcoal.
+100	No gelation MgO, PbO, PbO_2, Pb_3O_4, P (red), $(CH_3COO)_2Mn$, $(CH_3COO)_2Pb$, Se, NaOH, KOH.
+300	No gelation MnO, Na_2O_2, Na_2HAsO_3, $NaHSO_3$, $NaNO_2$, As_2O_3, S_2Cl_4, Na_2S, $Na_2S_2O_3\cdot 5H_2O$, $MgCl_2\cdot 6H_2O$.

Generally basic substances have strong gelation retarding actions.

Next, about the effects of sulphur and selenium, experiments were carried out in more detail. It is known that sulphur and selenium have special chemical action (a kind of isomerisation) upon the drying oil[1], but no report has been published about the effects upon the gelation of tung oil.

I. Effect of Sulphur. As it was difficult to mix sulphur in tung oil uniformly, the carbon disulphide solution of sulphur was added and after

(1) T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.* London, **58** (1939), 233; H. I. Waterman, C. Van Vlodrop, F. Althiusius, *ibid.*, **57** (1938), 87; J. Rinse, *Rec. trav. Chim.*, **51** (1932), 529.

Table 4.

Time lapsed from addition of sulphur (min.)	Gelation time (sec.)
30	1337
60	1366
90	1411
150	1426
210	1454
270	1478

evaporating the solvent the measurements were carried out at 270°C. by usual method.

In Table 4 the results of gelation times of tung oil added with 0.013% of sulphur were given. The gelation time increases with the lapse of time from addition of sulphur.

In the following experiments the measurements were done at 30 min. after addition of sulphur.

Table 5. (Tung oil 100%).

Amount of S (%)	Gelation time (t)	$\frac{1}{t}\times10^4$	log t
0	830	12.05	2.919
0.005	1032	9.69	3.014
0.010	1212	8.25	3.084
0.015	1404	7.12	3.147
0.020	1586	6.32	3.200
0.025	1793	5.58	3.254
0.030	2018	4.97	3.305

Table 6. (Tung oil 95%, Soya bean oil 5%).

S (%)	t	$\frac{1}{t}\times10^4$	log t
0	855	11.69	2.932
0.005	1139	8.77	3.057
0.010	1379	7.24	3.139
0.015	1680	5.95	3.225
0.020	1896	5.29	3.278
0.025	2311	4.32	3.364
0.030	2567	3.90	3.409

Table 7. (Tung oil 90%, Soya bean oil 10%).

S (%)	t	$\frac{1}{t}\times10^4$	log t
0	1125	8.89	3.051
0.005	1307	7.62	3.116
0.010	1671	5.95	3.223
0.015	1970	5.06	3.295
0.020	2446	4.00	3.388
0.025	2838	3.52	3.453
0.030	3436	2.90	3.536

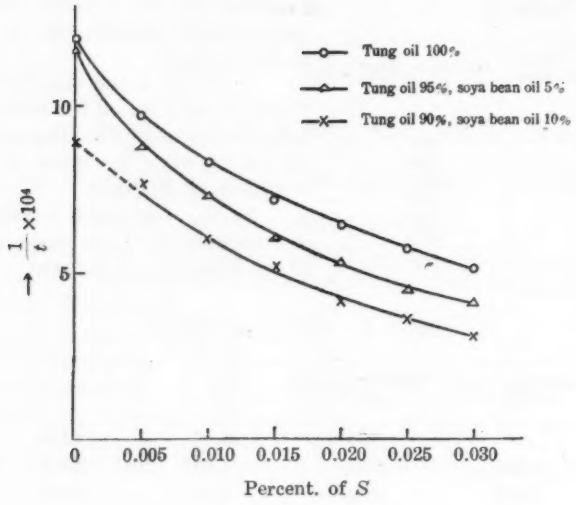


Fig. 1.

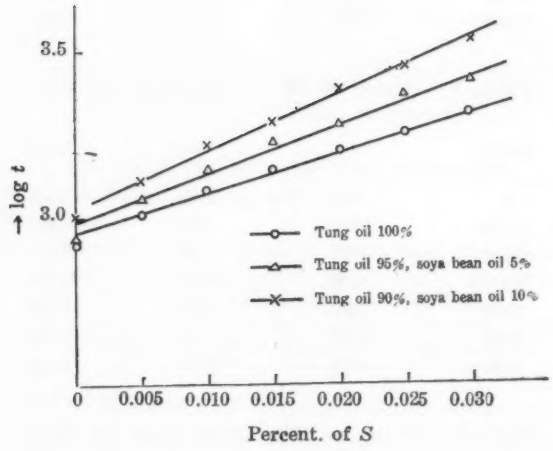


Fig. 2.

As shown in Fig. 1, from the relations between $1/t$ and x curved lines were obtained. In Fig. 2 relations of log t–x were shown. Except the initial points linear relations were obtained.

II. Effect of Selenium. The experiments were conducted as same as that of sulphur. In this case the solvent was not evaporated off, but the blanc test was done (Table 8).

Table 8. Effect of carbon disulphide.

Amount of carbon disulphide (g./5 g. tung oil)	%	t
0	0	1024
0.1	2	1090
0.2	4	1155
0.3	6	1200
0.4	8	1220
0.5	10	1245
0.6	12	1280
0.7	14	1310
0.8	16	1335
0.9	18	1352

The solvent has a little gelation retarding action.

Table 9. (Tung oil 100%).

Amount of solution added (g.)	Se (%)	t	$\frac{1}{t}\times 10^4$	$\log t$
0	0	1018	9.82	3.008
0.5	0.0139	1646	6.08	3.216
0.6	0.0167	1860	5.38	3.270
0.7	0.0195	1980	5.05	3.297
0.8	0.0222	2165	4.62	3.336
0.9	0.0250	2397	4.17	3.380
1.0	0.0278	2640	3.99	3.422
2.0	0.0556	5400<	1.85>	3.73<

Table 10. (Tung oil 95%, Soya bean oil 5%).

Amount of solution added (g.)	Se (%)	t	$\frac{1}{t}\times 10^4$	$\log t$
0	0	1130	8.85	3.053
0.1	0.0027	1355	7.38	3.131
0.3	0.0082	1718	5.82	3.235
0.4	0.0110	2052	4.87	3.312
0.5	0.0137	2240	4.46	3.351
0.7	0.0192	3090	3.24	3.481
0.9	0.0247	4170	2.40	3.620

Table 11. (Tung oil 90%, Soya bean oil 10%).

Amount of solution added (g.)	Se (%)	t	$\frac{1}{t}\times 10^4$	$\log t$
0	0	1300	7.69	3.114
0.1	0.0028	1695	5.89	3.229
0.2	0.0056	2122	4.71	3.328
0.3	0.0083	2430	4.12	3.386
0.5	0.0140	3275	3.05	3.515
0.6	0.0168	3780	2.65	3.578
0.7	0.0196	4565	2.19	3.659

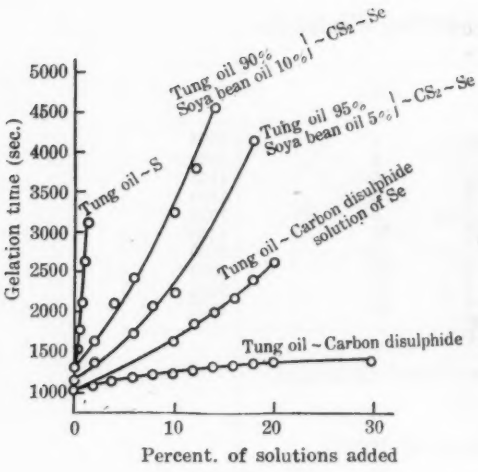


Fig. 3.

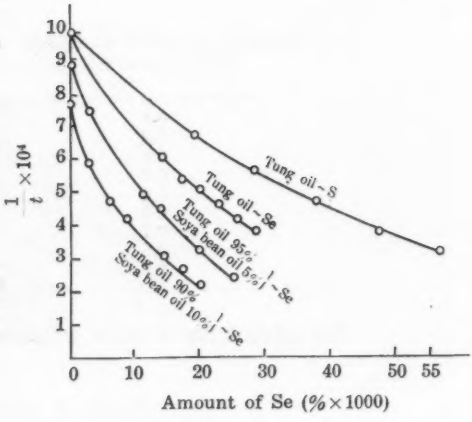


Fig. 4.

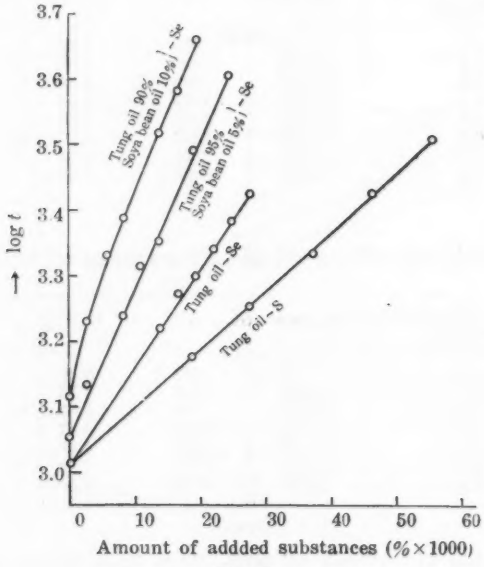


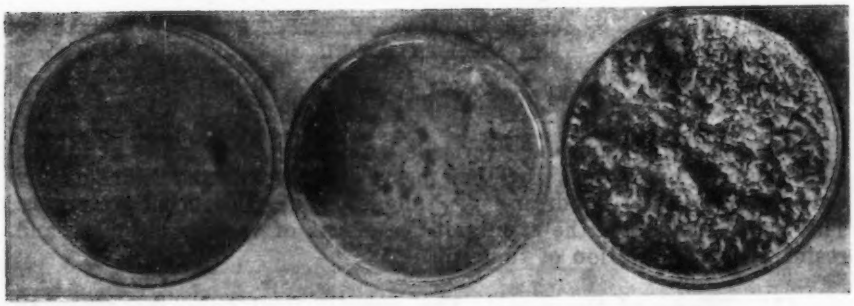
Fig. 5.

The comparison of the effects of sulphur and selenium with the same conditions was shown in Fig. 4. Selenium has stronger gelation retarding action than sulphur.

III. Isomerisation. Isomerisation of tung oil by S, Se and I_2 were examined. 10 g. of tung oil was taken in a glass dish (80, 15h) and irradiated by a ultraviolet lamp (100–110 V. 4 A.), distance of lamp and sample being 35 cm.

The photographs of tung oil added with 0.05% of reagents, after irradiation of 10 hours, were shown in Fig. 6.

Iodine has the strongest isomerisation power and the next is selenium.



Selenium Sulphur Iodine

Fig. 6.

Summary.

(1) As inorganic reagent besides sulphur and selenium, 16 kinds of elements, 28 of halides, 18 of nitrates, 23 of sulphates, 17 of oxides and 29 of other miscellaneous substances were used. Many of the halides have strong gelation accelerating actions and magnesium compounds have strong gelation retarding actions.

Metallic sodium acts gelation accelerating and manganese, compounds which are used as oxidation catalysers in paint industry, act as gelation retarding catalysers. Generally speaking acidic substances have gelation accelerating and basic substances have gelation retarding action.

(2) Gelation retarding power of S and Se are very strong and the gelation time of tung oil becomes infinitely long when added with 0.05% of regents. At the same concentration the gelation retarding action of Se is stronger than that of S.

(3) The relation between the logarithm of gelation time and the amount of S added is linear. These results can be applied also to the systems of mixture of tung oil and soya bean oil.

(4) S, Se and I_2 have isomerisation action upon tung oil at room temperature when irradiated by ultraviolet light.

(5) The gelation time of tung oil increases with the lapse of time from addition of S, so there is an intimate connection between the isomerisation and the gelation retarding action.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

Laboratory of Hitachi Works, Hitachi Ltd.

Polymerisation of Tung Oil. VIII. Effects of Various Bitumens and Resins upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

The insulating varnishes are made by cooking the mixture of drying oils, bitumens and resins, and their properties are affected eminently by the cooking process. As drying oils, tung oil is one of the most preferable. This paper deals with the results of the effects of various bitumens and resins upon the gelation of tung oil.

(I) Effects of Bitumens. The samples used have the following constants (Tables 1, 2).

Table 1.

Constants of petroleum asphalts.

Kind of Asphalts	Penetration degree (25°C., 100g., 5 sec.)	Softening point (°C.) (Ball & ring method)
S-1	6.0	72.5
S-2	40.7	52.0
S-3	70.0	51.0
B-1	7.0	126.5
B-2	29.0	69.0
B-3	33.5	66.0

S: Straight asphalt
B: Blown asphalt

Table 2.

Softening point of bitumens.

Names of bitumens	Softening point (°C.)
Gilsonite	150.5
Petroleum pitch	108.5
Stearin pitch	82.5
Mineral rubber	137.0
Coal tar pitch	121.0

The measuring methods were the same as those described in the previous reports, the determinations being carried out at 270°C. The relation between gelation time and percentage of petroleum asphalt added to tung oil is shown in Table 3.

Fig. 1 and Fig. 2 show the relation between reciprocals of gelation times ($1/t$) and percentages (x) of straight and blown asphalts added to tung oil.

As shown in these figures, the gelation of tung oil is promoted, when petroleum asphalt is added in an amount less than 10 percent.; but an addition of a larger amount of asphalt tends to prevent the gelation. This sort of inversion is a newly recognized fact. It seems that petroleum asphalt which has a lower softening point has somewhat greater retarding effect on the gelation.

Results with various bitumens are shown in the following.

The inversion was observed at 10% with samples containing gilsonite, mineral rubber, tar pitch, petroleum pitch, and at 25% with those containing stearin pitch.

Table 3. Gelation time of tung oil containing petroleum asphalts.

Kind of asphalts	Percent. of asphalt added (x)	Gelation time (sec.) (t)	$\frac{1}{t}\times 10^4$
S-1	0	938	10.66
	4.96	875	11.43
	9.96	866	11.55
	20.00	944	10.59
	29.82	1101	9.08
	39.90	1585	6.31
S-2	0	939	10.65
	5.00	881	11.35
	9.94	871	11.42
	19.96	973	10.28
	29.50	1228	8.14
	40.00	2398	4.17
S-3	0	937	10.67
	5.00	891	11.22
	9.82	907	11.03
	20.00	1014	9.86
	30.00	1208	8.28
	39.95	1766	5.66
	50.00	>3499	2.86>
B-1	0	938	10.66
	10	754	13.26
	20	799	12.52
	30	992	10.08
B-2	0	933	10.72
	10	798	12.53
	20	861	11.61
	30	1037	9.64
B-3	0	938	10.66
	10	861	11.62
	20	922	10.85
	30	1238	8.08

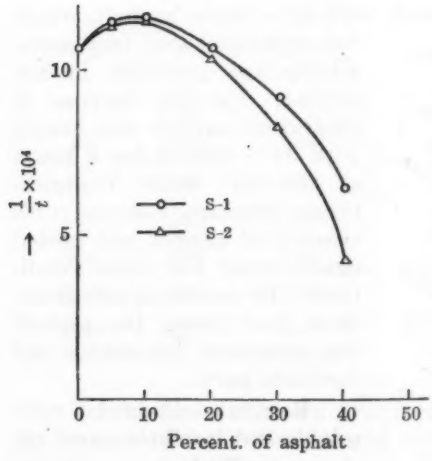


Fig. 1.

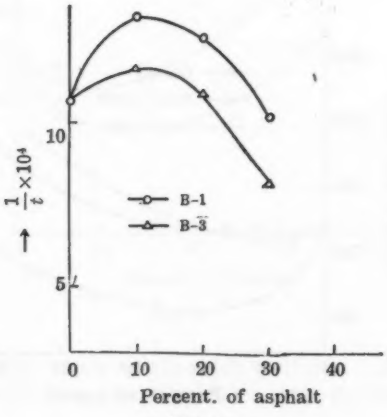


Fig. 2.

Table 4. Gelation time of tung oil containing bitumens.

Kind of bitumens	x (%)	t (sec.)	Kind of bituments	x (%)	t (sec.)
Gilsonite	0	782	Coal tar pitch	0	904
	4.96	752		5.0	870
	10.80	771		10.0	810
	15.31	781		14.9	836
	25.00	792		25.1	969
	35.30	849		35.1	1148
	45.10	953	Stearin pitch	0	776
	54.80	1108		4.96	618
Mineral rubber	0	785		9.95	551
	5.16	723		14.97	546
	9.94	734		24.85	543
	15.56	773		35.0	566
	24.00	814		44.9	649
	35.18	940		54.5	771
	45.00	1056	Petroleum pitch	0	920
	55.00	1447		5.0	764
				10.0	736
				15.0	755
				25.0	761
				35.0	947

The relation between components of asphalt and the inversion. As shown above, every bitumen added in small amount to tung oil promotes the gelation, where when the added amount increases the effect is reversed, and it retards the gelation. This is a phenomenon which is not found in cases of fatty oils, fatty acids, hydrocarbons, etc.

In order to study the relation between components of asphalt and the inversion, following two experiments were undertaken.

(1) The measurements were made with 15°– blown asphalt, which was separated into two parts, soluble and insoluble in hot alcohol. For the purpose of separation, asphalt was heated with 94% alcohol for 5 hours at 120–130° under 7 atmospheric pressure, followed with renewal of alcohol, and heated again under the same conditions. By repeating this treatment four times, the asphalt was separated into soluble and insoluble parts.

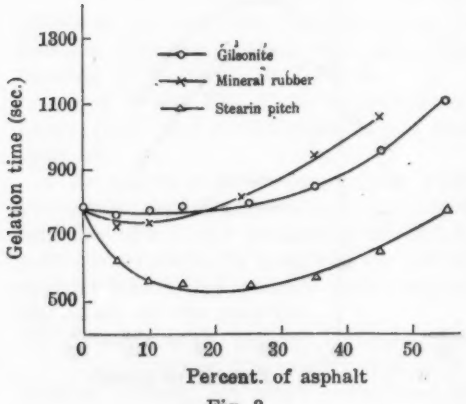


Fig. 3.

Results obtained with soluble and insoluble parts are shown in Table 5.

Table 5. Gelation time of tung oil containing 15°-blown asphalt.

15°-Blown asphalt	x (%)	t (sec.)	15°-Blown asphalt	x (%)	t (sec.)
Alcohol-insoluble part	0	871	Alcohol-soluble part	0	897
	5.0	843		5.0	810
	9.97	809		10.0	800
	14.97	870		14.75	799
	20.0	919		23.60	833
	25.0	998		26.10	894
	30.0	1117		30.00	997

The inversion occurs at 10% with tung oil containing alcohol-insoluble part of blown asphalt and at 15% with that containing alcohol-soluble part.

(2) The components of asphalt are not well known at present, but it is generally accepted that asphalt is composed of petrolen and asphalten. A solution of 5 g. of 5°-blown asphalt in 25 c.c. benzene was poured into 200 c.c. benzine. The precipitate thus obtained was collected and dried to give asphalten, and the filtrate was evaporated to an oily substance, petrolen.

Effects of the petrolen and asphalten upon gelation of tung oil were studied. Results with petrolen are given in Table 6.

Table 6. Gelation time of petrolen of 5°-blown asphalt.

x (%)	t (sec.)	$\frac{1}{t}\times 10^4$
0	917	10.91
5.0	1004	9.96
10.13	1181	8.47
15.0	1392	7.18
20.0	1826	5.48
24.93	2538	3.94
29.94	3671	2.72

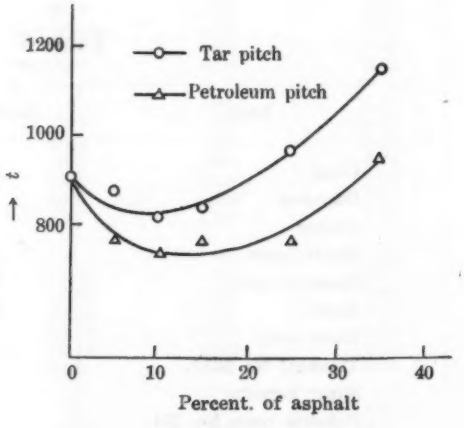


Fig. 4.

The inversion was not found in the experiments with petrolen. As in the case of fatty oils, $1/t$ and x were in a linear relation, and x_∞ was 38.0%.

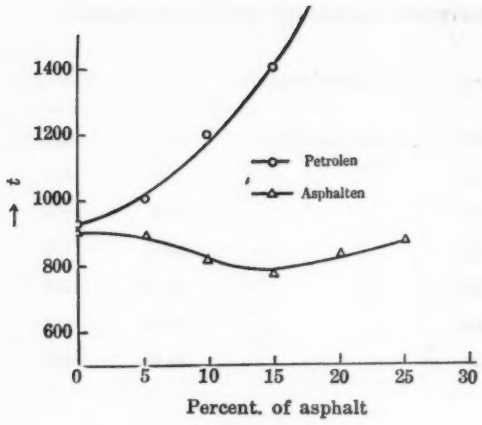


Fig. 5.

Table 7. Gelation time of tung oil containing asphalten of 5°-blown asphalt.

x (%)	t (sec.)
0	899
4.99	886
9.98	801
15.0	768
20.0	827
24.95	861

Results with asphalten are shown in Table 7. In this case the inversion occurred at 15%.

Of the substances reported only α-naphthol indicated the inversion. It can be anticipated that asphalten contains some substances giving a peculiar effect on tung oil.

(II) Effects of Various Resins. Next the effect of various natural and synthetic resins on gelation time of tung oil were examined. Acid values and iodine values of these resins are shown in Table 8.

Table 8.

Resin	Acid value	Iodine value
Copal	134	120.7
Dammar	31.2	83.5
Amber	20.5	61.4
Mastic gum	56.7	124.0
Sandarac gum	134	101.9
Rosin	132.4	130.9
Ester rosin	35.0	115.8
Tamanol No. 125 L	17.8	80.1
Super becacite	28.1	52.7
Bakelite resin No. 254	47.5	66.3
Leuchtol	4.7	55.1
Phthalate resin	7.6	80.4
Coumarone resin	0.5	31.8
Hitachi oil soluble resin	21.4	79.8

Each of these resins was pulverized, weighed, and put into test tubes and suitable quantities of tung oil were added; measurement was carried out at 270°C. in every case.

The gelation times in second were shown in Table 9.

Table 9.

Kind of Resins and Remarks	Addition x (%)	t (sec.)	$\frac{1}{t}\times 10^4$
(1) Copal: An approximately linear relation is found between $1/t$ and x and the value of x_∞ is 91.5%.	0	803	12.45
	4.98	891	11.22
	10 0	936	10.68
	15.1	999	10.00
	20.1	1073	9.32
	25.1	1142	8.75
	30.0	1254	7.97
(2) Dammar: The result is similar to that of copal and the value of x_∞ is 67%.	0	791	12.64
	4.99	857	11.67
	9.95	928	10.77
	14.9	1019	9.81
	19.9	1120	8.98
	24.95	1265	7.91
	30.0	1445	6.92
(3) Amber: The general tendency is the same as the above two resins and x_∞ is 62.5%.	0	88[illegible]	11.34
	4.97	935	10.70
	10.0	1029	9.27
	15.0	1141	8.76
	19.9	1313	7.62
	24.9	1503	6.65
	29.9	1658	6.03
(4) Mastic gum: A slightly curved line is obtained, x_∞ being 62.5%.	0	879	11.38
	5.36	954	10.48
	10.3	1016	9.84
	14.9	1111	9.00
	19.9	1259	7.94
	24.9	1430	6.99
	30.0	1693	5.91
(5) Sandarac gum: The value of x_∞ is approximately estimated to 87%.	0	892	11.21
	5.0	952	10.51
	10.0	988	10.12
	15.0	1084	9.22
	20.0	1118	8.95
	25.0	1228	8.14
	30.0	1394	7.17
(6) Coumarone resin: A straight line is obtained, x_∞ being 64.5%.	0	843	11.86
	4.99	924	10.82
	10.53	1004	9 96
	14.94	1088	9.19
	19.89	1173	8.52
	25.15	1382	7.23
	31.2	1661	6.02
(7) Ester rosin: A curved line is obtained and x_∞ is 42%.	0	889	11.25
	4.98	947	10.56
	9.96	1002	9.98
	15.0	1114	8.98
	20.0	1358	7.36
	25.0	1661	6.02
	30.0	2742	3.65

Table 9.—(*Concluded*)

Kind of Resins and Remarks	Addition x (%)	t (sec.)	$\frac{1}{t}\times10^4$
(8) Tamanol 125 L: $1/t$ and x bear an irregular relation, this may be probably due to the less soluble nature of the resin in tung oil and the value of x_∞ estimated is 120%.	0	917	10.91
	5.11	927	10.79
	10.0	956	10.46
	13.88	972	10.29
	20.0	1060	9.43
	25.0	1120	8.93
	30.0	1265	8.58
(9) Super beckacite: A slightly gelation-accelerating action is observed.	4.98	909	10.98
	9.90	953	10.49
	14.94	932	10.74
	19.84	904	11.06
	23.97	866	11.55
	29.46	798	12.53
(10) Phthalate resin: A curved line is obtained and the value of x_∞ is less than 60%.	4.90	923	10.83
	10.0	948	10.55
	14.59	978	10.22
	19.92	1034	9.67
	25.00	1055	9.48
	29.64	1128	8.87
(11) Leuchtol: The gelation-preventing action is very strong and the value of x_∞ is approximately 22%.	5.0	928	10.78
	9.83	1062	9.42
	14.74	1554	6.43
	20.0	3642	2.74
(12) Bakelite resin No. 254: An irregular relation, probably due to its less soluble nature in tung oil, is obtained.	0	848	
	5.0	809	
	9.84	751	
	14.76	742	
	19.92	728	
	24.5	761	
	30.0	848	
(13) Oil soluble phenol-formaldehyde resin made by Hitachi Works: The result is the same as above.	0	882	
	4.6	866	
	9.8	889	
	14.9	938	
	19.7	922	
	24.0	942	
	29.7	988	

(14) Rosin:

In order to find the gelation-retarding effect of rosin the following experiments were carried out.

Table 10. Gelation time at 250°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	1910 (t_0)	5.236	—
5	1954	5.118	0.0256
10	2095	4.773	0.0463
15	2301	4.346	0.0593
20	2582	3.873	0.0682
25	3120	3.205	0.0812

Table 11. Gelation time at 260°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	1324	7.553	—
5	1366	7.321	0.0044
10	1460	6.849	0.0704
15	1563	6.277	0.0857
20	2039	4.904	0.1325
25	3030	3.300	0.1701

Table 12. Gelation time at 270°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	955	10.47	—
5	985	10.17	0.060
10	1066	9.38	0.109
15	1250	8.00	0.164
20	1598	6.26	0.210
25	3025<	—	—

Table 13. Gelation time at 290°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	441	22.68	—
5	491	20.37	0.462
10	574	17.42	0.526
15	753	13.28	0.621
20	1371	7.29	0.769
25	3720<	2.69>	0.800<

Table 14. Gelation time at 300°C.

x (%)	t (sec.)	$\frac{1}{t}\times10^4$	$\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)\times10^4$
0	365	27.4	—
5	397	25.2	0.442
10	510	19.6	0.779
15	703	14.2	0.878
20	2203	4.54	1.143
25	4800<	2.08	—

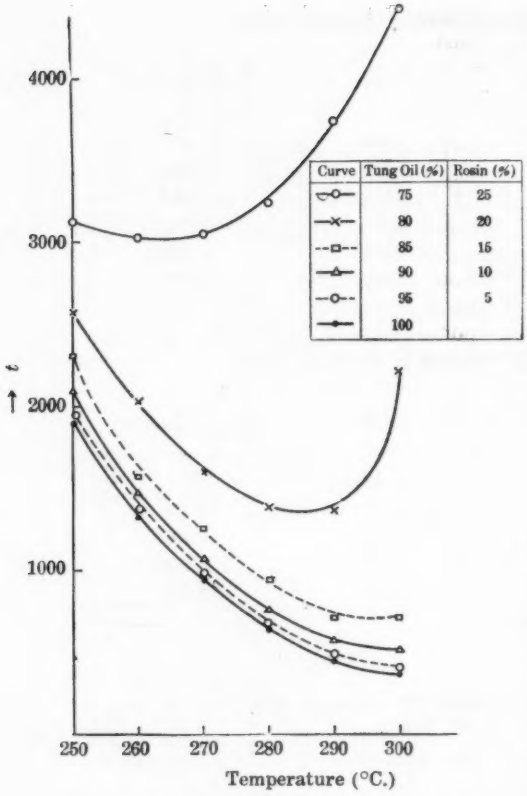


Fig. 6. Relation between Gelation-time and Temperature

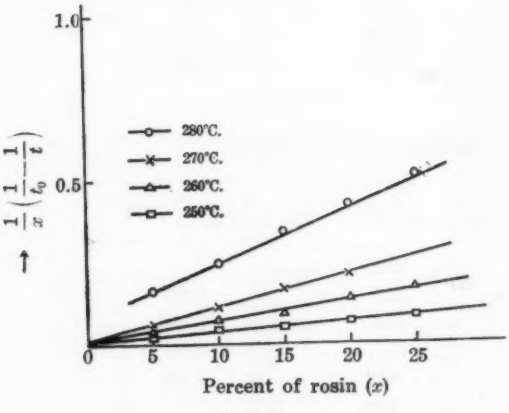


Fig. 7.

The relations between gelation time and temperature are shown in Fig. 6.

The general tendency is the same as that of fatty acid.

The relations between $\frac{1}{x}\left(\frac{1}{t_0}-\frac{1}{t}\right)$ and x are shown in Fig. 7.

From Fig. 7 it is noticed that the reciprocals of gelation time $(1/t)$ may be expressed by the quadratic equation of x.

Summary.

(1) Studies on the effects of straight asphalts, blown asphalts, gilsonite, petroleum pitch, stearin pitch, mineral rubber, coaltar pitch, etc. on the gelation time of tung oil lead to the conclusions that the gelation is promoted with bitumen added in an amount less than 10–15 percent., but is prevented with an addition of larger amount of bitumen. The inversion was noticed as the amount of substances added increase.

(2) Petroleum asphalt with a lower softening point has a somewhat greater gelation preventing effect.

(3) 15° blown asphalt was separated into alcohol soluble and insoluble parts. As in the case of the original asphalt, the inversion was found in the experiments with the soluble and insoluble parts.

(4) 5° blown asphalt was separated into asphalten and petrolen, and effects on gelation were studied. As in the case of ordinary neutral substances, the linear relation of $1/t$ and x was observed in the experiments with petrolen, but as in the case with original asphalt, the inversion was noticed when asphalten was used.

(5) The gelation-retarding effects of various natural and synthetic resins were observed. Among them copal, dammar, amber, coumarone resin have retarding effects, and $1/t$ and x bear a linear relation.

The relation $1/t$ and x for mastic, leuchtol, phthalate resin, ester rosin, sandarac, tamanol are not linear.

Generally speaking, the relations of $1/t$ and x for neutral and soluble resins are linear, but those of the less soluble resins are not linear.

About the effect of rosin upon gelation of tung oil, many measurements were carried out and the relation of $1/t$ and x are shown to be expressed by a quadratic equation. The influence of temperature on the gelation times of tung oil mixed with rosin is similar to that of fatty acid.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. Yokota for their kind guidance.

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Studies on Reactions between Gas and Solid. VII. Nitrogenation of Calcium Carbide and Its Kinetic Discussion.

By **Takeo AONO.**

(Received February 24, 1941.)

Introduction. The velocity of nitrogenation of calcium carbide had been experimentally determined as functions of pressure, temperature, size of grain and catalysers, and was formerly reported.[1][2][3][4] Some theoretical discussions upon this reaction kinetics will be given here.

Gas-Solid Reaction. The carbide which was used in these experiments* did not melt or sinter till about 1100°C when heated in vacuum for some time. When the carbide was subjected to the reaction with nitrogen the product sintered very slightly at the furnace temperature above 950°C; and the local melting was perceived above 1150°. At 870°C of the furnace temperature even slight sintering was not perceived.

(1) T. Aono, this Bulletin, **7** (1932), 143–154.
(2) T. Aono, *ibid*, 247–255.
(3) T. Aono, *ibid*, 274–280.
(4) T. Aono, *ibid*, 287–297.
* Technical carbide powder of the composition 68.2% CaC_2, 1% CaF_2.

Therefore, beneath the furnace temperature of about 950°C, it can be thought that nitrogen is acting upon solid carbide to form solid products. In this range of temperature the reaction mechanism can be considered as follows.

The first step of the reaction will be the adsorption of nitrogen on some active spots of the carbide. Being higher temperatures the adsorption will chiefly be of chemical or activated nature and an adsorption compound, say $CaC_2 \cdot N_2$, will be formed temporarily. Some of such a compound, with an energy larger than the heat of activation, will change to $Ca(CN)_2$; others will break up again into carbide and nitrogen. The $Ca(CN)_2$, thus formed, can exist also temporarily, because at such temperatures the cyanide is very unstable and goes into $CaCN_2$ and C.[5] The reaction scheme is given as follows.

$$\underset{(gas)}{N_2} + \underset{(solid)}{Carbide} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{(say\ CaC_2 \cdot N_2)}{Adsorption} \underset{k_4}{\overset{k_3}{\rightleftarrows}} Ca(CN)_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} CaCN_2 + C\,.$$

$$(P) \qquad (S) \qquad (\sigma) \qquad (\rho) \qquad (\delta)$$

Equations of the reaction velocity. Let us use the following notations:

- S: the total (effective) active spots capable of formation of the adsorption compound, at time t,
- σ: position occupied by the adsorption compound, say $CaC_2 \cdot N_2$,
- ρ: quantity of effective $Ca(CN)_2$,
- δ: quantity of effective $CaCN_2$,
- k_1: velocity constant of condensation of nitrogen,
- k_2: velocity constant of evaporation of nitrogen,
- k_3: velocity constant of $Ca(CN)_2$-formation from adsorption compound,
- k_4: velocity constant of back formation of adsorption compound from $Ca(CN)_2$,
- k_5: velocity constant of formation of $CaCN_2+C$ from $Ca(CN)_2$,
- k_6: velocity constant of formation of $Ca(CN)_2$ from $CaCN_2+C$,

all being taken in proper units. Assuming the law, which resembles that of mass-action, to hold in this case, the following equations can be written down:

$$-\frac{dN}{dt} = k_1 P(S-\sigma) - k_2\sigma \qquad (1),$$

$$\frac{d\sigma}{dt} = -\frac{dN}{dt} - k_3\sigma + k_4\rho \qquad (2),$$

$$\frac{d\rho}{dt} = k_3\sigma - k_4\rho - k_5\rho + k_6\delta \qquad (3),$$

(5) The formation of $Ca(CN)_2$ was varified by the author experimentally, and this will be discussed later. It was also reported by H. H. Franck and his co-workers in *Z. Elektrochem.* **45** (1939), 541.

$$\frac{d\delta}{dt} = k_5\rho - k_6\delta \qquad (4),$$

and

$$-\frac{dN}{dt} = \frac{d\sigma}{dt} + \frac{d\rho}{dt} + \frac{d\delta}{dt} \qquad (5),$$

where $-\frac{dN}{dt}$ means the rate of decrease of the gaseous nitrogen by means of the above change, and P means the pressure of nitrogen. Adsorption other than the above chemical one must also be existing, but owing to the high temperature the quantity of such will be small, and moreover, the velocity of condensation and evaporation of such kind of adsorption will be very fast, and we can consider that this kind of adsorption is always in a stationary state. Therefore the decrease of gaseous nitrogen will practically be due to the above change.

From Equations (1) and (2) we have

$$\frac{d\sigma}{dt} = (k_1PS + k_4\rho) - (k_1P + k_2 + k_3)\sigma \qquad (6),$$

and then

$$\sigma = e^{-\int(k_1P+k_2+k_3)dt}\left\{\int(k_1PS + k_4\rho)\, e^{\int(k_1P+k_2+k_3)dt}dt + const.\right\}$$

$$= e^{-Kt}\left\{\int(k_1PS + k_4\rho)\, e^{Kt}dt + const.\right\} \qquad (7),$$

where $K = k_1P + k_2 + k_3$.

At constant temperature and pressure k_1, k_2, k_3, k_4, k_5, k_6 and P must all be constant. S is, of course, a function of time. From the experimental evidence reported formerly by the author[2][3][4], this change seems to be of a kind of auto-catalysis, and if we assume the following scheme:

Inactive carbide $\xrightarrow{k}$ active carbide $\xrightarrow{k_1P}$ adsorption compound, we have
(S_i) (S) (σ)

$$-\frac{dS_i}{dt} = kS_i\,; \qquad S_i = S_{i0}\,e^{-kt} \qquad (8),$$

where $S_{i0} = S_i$ at $t = 0$.

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(6) The "Active and inactive" have two meanings:
a) in case of reaction with nitrogen and solid carbide, the ordinary position is inactive, while the position adjascent to the produced nascent carbon and cyanamide or the activator, and which has the properties of fixing the nitrogen in active. The reaction will proceed principally along the contact places, that is, the active position.
b) in case of reaction with nitrogen and carbide at higher temperatures, the carbide dissolves into the products and becomes easier to react with the nitrogen. Therefore in this case the "active" means the dissolved and activated carbide.

$$\frac{dS}{dt} = kS_i - k_1PS \qquad (9),$$

from which

$$S = \frac{S_{i0}}{k_1P-k} \cdot e^{-kt} - \left(\frac{S_{i0}}{k_1P-k} - S_0\right) e^{-k_1Pt} \qquad (10),$$

or

$$S = S_0' e^{-kt} - (S_0' - S_0) e^{-k_1Pt} \qquad (10'),$$

where

$$S_0' \equiv S_{i0}/(k_1P-k) .$$

From (10) and (7) we have

$$\sigma = \sigma_0 e^{-Kt} + k_1P\left\{\frac{S_0'}{K-k}(e^{-kt} - e^{-Kt}) - \frac{S_0'-S_0}{K-k_1P}(e^{-k_1Pt} - e^{-Kt})\right\} \qquad (11),$$

because, at the earlier stage of the reaction, where the change is proceeding from the left to the right, $k_4\rho$ must be very much smaller than k_1PS and can be neglected.

S_0 and σ_0 represent the values of S and σ at $t=0$. (See Fig. 1).

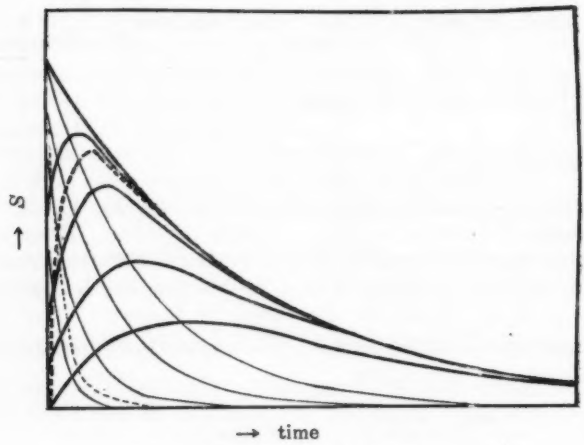

Fig. 1. Curves for "S."

Introducing Eq. (11) into (1) we have

$$-\frac{dN}{dt} = \frac{k_1(k_3-k)PS_0'}{K-k} e^{-kt} - \frac{k_1P(k_3-k_1P)(S_0'-S_0)}{k_2+k_3} e^{-k_1Pt}$$

$$-(k_1P+k_2)\left\{\sigma_0 - k_1P\left(\frac{S_0'}{K-k} - \frac{S_0'-S_0}{k_2+k_3}\right)\right\} e^{-Kt} \qquad (12).$$

This equation (12) gives the rate of nitrogen fixation provided that the reaction products affecting no retarding effect to the reacting sub-

stances. The characteristics of the reaction velocity-time curves found by the experiments coinside with this Eq. (11)[2][3].

Effect of pressure. By studying the reaction in its comparatively earlier stage, whereby the influence of the layer of the product was small, it was also found by the author[1] that at a constant temperature the velocity of this reaction is not directly proportional to the pressure of nitrogen but the following relation exists.

$$-\frac{dP}{dt} = \kappa\frac{P}{1+aP} \equiv \frac{P}{aP+b} \qquad (13),$$

where $\varkappa$ and a or a and b being constants. This relation can also be derived from the above equations.

During a short time of measurement at such a lower temperature of nitrogenation as in those experiments, S can be taken as constant and $k_4\rho$ can be neglected against k_1PS, then from Eq. (7) we have

$$\sigma = \sigma_0 e^{-Kt} + \frac{k_1}{K}PS\left\{1-e^{-Kt}\right\} \qquad (14),$$

After a sufficient time e^{-Kt} becomes sufficiently small and then we have

$$\sigma_\infty = \frac{k_1}{K}PS = \frac{k_1PS}{k_1P+k_2+k_3} \qquad (15),$$

and from (1).

$$-\frac{dN}{dt} = \frac{k_1k_3PS}{k_1P+k_2+k_3} \qquad (16).$$

This relation is also obtained by putting

$$-\frac{dN}{dt} = k_1P(S-\sigma_\infty)-k_2\sigma_\infty = k_3\sigma_\infty \qquad (17),$$

which means that the decrease of gaseous nitrogen is merely due to the chemical change, that is, $\frac{d\sigma}{dt} = 0$.

For a constant gaseous space (v) the decrease of nitrogen is proportional to the decrease of pressure and we have from (16)

$$-\frac{dN}{dt} = -v\frac{dP}{dt} = \frac{k_1k_3PS}{k_1P+k_2+k_3},$$

$$\therefore \quad -\frac{dP}{dt} = \frac{P}{\left(\frac{v}{k_3S}\right)P+\left(\frac{k_2+k_3}{k_1k_3S}\right)v} \equiv \frac{P}{aP+b} \qquad (18)$$

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(1),(2),(3): *loc. cit.*

or

$$-\frac{dP}{dt}=\frac{k_1k_3S}{(k_2+k_3)v}\cdot\frac{P}{\left(\frac{k_1}{k_2+k_3}\right)P+1}\equiv\kappa\frac{P}{aP+1} \qquad (18')$$

where

$$\left.\begin{aligned}\kappa&=\frac{k_1k_3S}{(k_2+k_3)v}, & a&=\frac{k_1}{k_2+k_3}=\frac{a}{b}\\ a&=\frac{v}{k_3S}, & b&=\left(\frac{k_2+k_3}{k_1k_3S}\right)v\end{aligned}\right\} \qquad (19).$$

The relations (18), (18′) coinside with (13) which was experimentally obtained.

Heat of Activation. From Equation (19) we have

$$\frac{1}{a}=\frac{S}{v}k_3 \qquad (20),$$

and as k_3 represents the reaction velocity between adsorbed nitrogen and carbide, its temperature function will be given as

$$k_3=A\cdot e^{-\frac{E}{RT}} \qquad (21),$$

and then for constant S we have

$$\frac{1}{a}=A'\cdot e^{\frac{E}{RT}} \qquad (22).$$

Therefore, if the above postulations are not wrong, $\log\left(\frac{1}{a}\right)$ will stand in linear relation with $\frac{1}{T}$ and the inclination of this line to the $1/T$ axis will give the value of $(-E/R)$, from which the temperature increment E can be calculated. From the experimental data reported in the former paper[1] we have Table 1 and Fig. 2.

Table 1.

Temp. °C	790	869	946	1008
a	4.07	1.36	0.125	0.022
$\frac{1}{T}\times10^3$	0.940	0.876	0.820	0.781
$\log_{10}\left(\frac{1}{a}\right)$	−0.609	−0.133	0.903	1.657

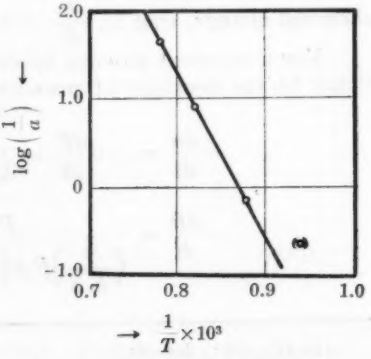

Fig. 2. Temperature increment.

Points except at the temperature of 790°C fall in a straight line, which proves the above postulation to be plausible. (The point of 790°C cannot be compared with the others, because this was taken from the measurement just at the beginning of the reaction, and which, as was formerly reported,[2][3] is a period of very abnormal). From the inclination of the line we have $E \approx 86$ Cal./mol., which must be the heat of activation for the reaction of adsorbed nitrogen and calcium carbide to form calcium cyanide.

Other reaction formulae. The equations derived above are to be available for the fixation of nitrogen by very fine powder of carbide, the reaction products affecting no retarding effect to the contact between the reacting substances.

When the grain of carbide is larger, or when the temperature is high enough to make the product sinter or melt, the reaction must occur between the carbide and nitrogen which has come through the product layers. Some of the velocity formulae were already derived and discussed in the preceding papers; and was also mentioned there that it is commonly difficult to represent the complete velocity course, experimentally found, with a single equation. This will partly be due to elevation of the local temperature by dint of the reaction heat, which changes the velocity constants during the course of the reaction, and partly because the products change their physical properties during the process due to the change of temperature.

Summary.

(1) From the experimental study of the nitrogenation of calcium carbide the author concluded its mechanism to be as follows:

(a) adsorptions of nitrogen on the carbide,

(b) formation of intermediate compound $Ca(CN)_2$ temporarily,

(c) breaking of $Ca(CN)_2$ into $CaCN_2$ and C.

(2) Equations for this (gas-solid) reaction velocity were derived from the above view. For constant temperature and pressure

$$-\frac{dN}{dt} = \frac{k_1P(k_3-k)S_0'}{K-k}e^{-kt} - \frac{k_1P(k_3-k_1P)(S_0'-S_0)}{k_2+k_3}e^{-k_1Pt}$$

$$-(k_1P+k_2)\left\{\sigma_0 - k_1P\left(\frac{S_0'}{K-k} - \frac{S_0'-S_0}{k_2+k_3}\right)\right\}e^{-Kt}$$

and for changing pressure

$$-\frac{dN}{dt} = \frac{k_1k_3PS}{k_1P+(k_2+k_3)}$$

$$-\frac{dP}{dt} = \frac{P}{aP+b}.$$

(3) The coincidence of these equations with the experimental results were discussed.

(4) The heat of activation for the reaction of the adsorbed nitrogen and carbide to form calcium cyanide was calculated to be approximately 86 Cal./mol.